

“The Diffusion of Ions into Gases.” By JOHN S. TOWNSEND, M.A. (Dublin), Clerk Maxwell Student, Cavendish Laboratory, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received April 25,—Read May 18, 1899.

(Abstract.)

In the paper upon this subject, the principles upon which the theory of interdiffusion of gases depends, are applied to the diffusion of ions produced by Röntgen rays. When a gas has been left to itself, the conductivity gradually disappears. When no electromotive forces are acting, the loss of conductivity is due partly to positive and negative ions coming into contact with each other, and partly to the effect of the surface of the vessel, which discharges those ions which come into contact with it.

In order to illustrate in a simple way the principles which are involved, we take the case of a gas contained in a metal sphere, and consider what happens to the ions after the gas has been removed from the influence of the rays. For present purposes we may neglect the effect of recombination.

The ions may be considered as constituting a separate gas, the molecules of which may be either bigger or smaller than the molecules of the gas in which they are immersed. When an ion comes into contact with the surface of the sphere it loses its charge, so that the metal may be regarded as a body which completely absorbs the ions. The reduction in the conductivity by the diffusion of the ions to the sides, is exactly analogous to the removal of moisture from a gas by bubbling it through sulphuric acid. The more rapidly the water vapour diffuses through the gas, the greater will be the number of water molecules which come into contact with the acid round the bubble. If the quantity of moisture which is removed be found experimentally, the coefficient of diffusion of water vapour into the gas can be deduced.* It would be impracticable to use this method to find the coefficient of diffusion of ions into a gas contained in a large vessel, as the loss of conductivity due to recombination would be large compared with the loss due to the sides.

The method which was employed was to pass a uniform stream of gas through fine metal tubing, and to allow the rays to fall on the gas immediately before entering the tubing. The bore of the tubing can be so adjusted that the number of ions which come into contact with the sides will be large compared with the number which recombine. It is convenient to use tubing of such a length, that the conductivity will be reduced to about one half its initial value.

* John S. Townsend, ‘Phil. Mag.’, June, 1898.

In order to obtain the coefficient of diffusion when the reduction in the conductivity has been found experimentally, the following problem presents itself :—

If a small quantity of a gas, A, is mixed with another gas, B, and the mixture passed along a tube, the sides of which completely absorb A, to find what quantity of A emerges from the tube with B.

It will be immediately seen that if the gases diffuse rapidly into each other, a large proportion of the molecules of the gas A will come into contact with the surface of the tube and will there be absorbed. If on the other hand the rate of interdiffusion is very small, the molecules of A will travel down the tube in straight lines parallel to the axis of the tube, and practically none of them will come into contact with the surface.

The complete solution of the above problem may be obtained from the following equations :—

$$\frac{1}{\kappa} pu = -\frac{dp}{dx} + nXe,$$

$$\frac{1}{\kappa} pv = -\frac{dp}{dy} + nYe,$$

$$\frac{1}{\kappa} pw = -\frac{dp}{dz} + nZe + \frac{1}{\kappa} pW,$$

and the equation of continuity $\frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0$; where n is the number of ions per cubic centimetre; p their partial pressure; e the charge on each ion; X, Y, and Z the electric forces at any point; u , v , and w the velocities of the ions; W the velocity of the gas B through the tube; κ the coefficient of diffusion of the ions into the gas B.

The partial differential coefficient with respect to the time, is omitted from the equation of continuity, as we need only consider the steady state.

The term dp/dz may be omitted from the third equation, as it is small compared with the other terms.

$W = \frac{2V}{a^2}(a^2 - r^2)$, where V is the mean velocity of the gas B, defined by the condition $\pi a^2 V t =$ total volume of gas crossing any section in a time t , a the radius of the tube, and r the perpendicular distance of any point from the axis.

The forces X, Y, Z vanish since the electrification is too small to contribute appreciably to the motion of the ions.

The boundary conditions are :—

$$p = 0 \text{ when } r = a,$$

$$p = \text{constant when } z = 0.$$

The solution of the problem requires a somewhat lengthy analysis, so that we give here only the final result.

The ratio of the number of ions (or molecules of the gas A) coming out of the tube with B to the number which enter is

$$R = 4 \left[0.1952 \epsilon^{-\frac{7.313\kappa z}{2a^2V}} + 0.0243 \epsilon^{-\frac{44.5\kappa z}{2a^2V}} + \&c. \right],$$

where z is the length of the tube.

The other terms of the series are too small to be taken into consideration.

Having determined the reduction in conductivity, due to tubes of different lengths, the following values of the coefficients of diffusion of ions into air, oxygen, carbonic acid, and hydrogen, were obtained.

Table of Coefficients of Diffusion of Ions in dry Gases.

Gas.	κ for + ions.	κ for - ions.	Mean value of κ .	Ratio of the values of κ .
Air	0.0274	0.042	0.0347	1.54
Oxygen	0.025	0.0396	0.0323	1.58
Carbonic acid.....	0.023	0.026	0.0245	1.13
Hydrogen	0.123	0.190	0.156	1.54

Table of Coefficients of Diffusion of Ions in moist Gases.

Gas.	κ for + ions.	κ for - ions.	Mean value of κ .	Ratio of the values of κ .
Air	0.032	0.035	0.0335	1.09
Oxygen	0.0288	0.0358	0.0323	1.24
Carbonic acid.....	0.0245	0.0255	0.025	1.04
Hydrogen	0.128	0.142	0.1350	1.11

We should expect from the experiments, that the above numbers were correct to 5 per cent.

Considering one of the equations of motion

$$\frac{1}{\kappa} pu = -\frac{dp}{dx} + nXe,$$

we see that when $dp/dx = 0$, the velocity u due to the electric force X is $nXe\kappa/p$. If the potential gradient is one volt per centimetre $X = 1/300$ in electrostatic units, and the corresponding value of u is

$$u_1 = \frac{\kappa e}{300} \cdot \frac{n}{p}.$$

Let N be the number of molecules in a cubic centimetre of a gas at pressure P , equal to the atmospheric pressure, and temperature 15° centigrade, the temperature at which u and κ were determined.

The quotient N/P may be substituted for n/p in the above equation, and since the atmospheric pressure P is 10^6 in C.G.S. units, we obtain

$$Ne = \frac{3 \times 10^8 u_1}{\kappa}.$$

The following values of Ne thus obtained for different gases are

Air	$Ne_A = 1.35 \times 10^{10}$
Oxygen	$Ne_O = 1.25 \times 10^{10}$
Carbonic acid	$Ne_C = 1.30 \times 10^{10}$
Hydrogen	$Ne_H = 1.00 \times 10^{10}$

The values of u were taken from the table of mean velocities given by Professor Rutherford.* The values of κ which were used, are the mean values obtained for dry gases.

Experiments on electrolysis show that one electrodynamic unit of electricity in passing through an electrolyte, gives off 1.23 c.c. of hydrogen at temperatures 15° and pressure 10^6 C.G.S. units. The number of atoms in this volume is $2.46 N$, so that if E is the charge on an atom of hydrogen in the liquid electrolyte,

$$\begin{aligned} 2.46NE &= 1 \text{ electrodynamic unit of quantity} \\ &= 3 \times 10^{10} \text{ electrostatic units.} \end{aligned}$$

Hence $NE = 1.22 \times 10^{10},$

the charge E being expressed in electrostatic units.

Since N is a constant, we conclude that the charges on the ions produced by Röntgen rays in air, oxygen, carbonic acid, and hydrogen, are all the same, and equal to the charge on the hydrogen ion in a liquid electrolyte.

Professor Thomson† has shown that the charge on the ions in hydrogen and oxygen which have been made conductors by Röntgen rays, is 6×10^{-10} electrostatic unit, and is the same for both gases.

Taking this value for the charge e , we obtain the number of molecules in a cubic centimetre of a gas

$$N = 2 \times 10^{19}.$$

From this we deduce the weight of a molecule of hydrogen, ρ/N ,

$$4.5 \times 10^{-24} \text{ gram.}$$

* E. Rutherford, 'Phil. Mag.,' November, 1897.

† J. J. Thomson, 'Phil. Mag.,' December, 1898.

Since, as we have shown, the charge on an ion produced by Röntgen rays is equal to the charge on a hydrogen ion in a liquid electrolyte, this latter charge is also 6×10^{-10} electrostatic unit.

Although the value of N_e for hydrogen is 25 per cent. less than its value for other gases, we are justified in including hydrogen in the above general conclusion, as we should expect the value of u for hydrogen to be too small. Professor Rutherford makes no mention of having corrected for the presence of air in his apparatus, or of having used perfectly dry hydrogen. If we take the mean value of κ for moist hydrogen, we obtain $N_{eH} = 1.15 \times 10^{10}$.

In order to prove that the charge on the positive ion is equal to the charge on the negative ion, the ratio of the coefficients of diffusion must be shown to be equal to the ratio of the velocities. Professor Zeleny* has shown that the negative ions travel faster under an electromotive force than the positive ions, the ratios of the velocities being 1.24 for air and oxygen, 1.15 for hydrogen, and 1.0 for carbonic acid.

The experiments on diffusion show that the ratio of the velocities would be larger in dry than in moist gases; but as this point has not yet been examined by Professor Zeleny, we cannot expect a very close agreement between the ratios which he gives for the velocities and the ratios of the coefficients of diffusion.

We are led to conclude that the charges on the positive and negative ions are equal from another point of view. It has been proved that the mean charge is the same as the charge on an ion of hydrogen in a liquid electrolyte. If the charges differed, one of them would be less than the charge on the hydrogen ion, whereas experiments on electrolysis show that all ionic charges are either equal to the charge on the hydrogen ion or an exact multiple of it.

“On the Presence of Oxygen in the Atmospheres of certain Fixed Stars.” By DAVID GILL, C.B., F.R.S., &c., Her Majesty’s Astronomer at the Cape of Good Hope. Received April 14,—Read April 27, 1899.

(PLATE 8.)

In a paper read before the Society on April 8, 1897, and in a subsequent paper,† Mr. Frank McClean draws attention to the grouping of lines other than those of helium and hydrogen in the spectra of β Scorpii, β Canis Majoris, β Centauri and β Crucis, suggesting that the close correspondence between the grouping of these extra lines and the known lines of oxygen, points to the probable presence of that gas in the atmospheres of these stars,

* J. Zeleny, ‘Phil. Mag.’ July, 1898.

† ‘Roy. Soc. Proc.’ vol. 42, No. 386, p. 418.